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Article

Diphenylphosphino- or Dicyclohexylphosphino-Tethered Boryl Pincer Ligands: Syntheses of PBP Iridium(III) Complexes and Their Conversion to Iridium−Ethylene Complexes

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Two hydroborane precursors (**1b**,**c**) for PBP pincer ligands bearing phenyl or cyclohexyl groups on phosphorus atoms were synthesized, and their complexation reactions with iridium were investigated. Reaction of hydroborane **1b**, bearing phenyl groups, with Ir[P(*p*-tol)$_3$]$_2$(CO)Cl afforded an 18-electron complex, [PhPBP]Ir(H)(CO)Cl (**3b**), but reactions with other iridium(I) sources gave complicated mixtures. The characteristic IR peaks in **3b** compared with the previously reported ^{t}Bu-PBP derivative **3a** were discussed on the basis of theoretical calculations. Complexation of cyclohexyl-substituted hydroborane **1c** with [Ir(C$_2$H$_4$)$_2$Cl]$_2$ afforded a 16-electron complex, [CyPBP]Ir(H)Cl (**2c**). X-ray structure and computational studies on **2c** revealed that the hydride ligand is close [B−H = 1.90(5) Å] to the boron atom. Reaction of **2c** with LiTMP (TMP = 2,2,6,6-tetramethylpipyridide) under ethylene atmosphere gave monovalent iridium complex [CyPBP]Ir(C$_2$H$_4$) (**4c**) by a similar procedure to the previously reported [^{t}BuPBP] system. Exposure of a CD$_2$Cl$_2$ solution of **2c** to ethylene without additional base resulted in a quantitative formation of the intermediate [CyPBP]Ir(H)(C$_2$H$_4$)Cl (**8c**), as was characterized by NMR spectroscopy. In contrast, no spectral change was observed in the same procedure using [^{t}BuPBP]Ir(H)Cl (**2a**) probably due to a difference in steric bulk. The observation of **8c** is a rare example of a spectroscopically identified boryl(hydrido)olefin metal complex.

Introduction

Transition metal boryl complexes[1−5] have been widely synthesized and applied to catalytic borylation reactions.[6−17] In all these reactions, boryl ligands act as "reactive" ligands. It is known that the boryl ligand has a higher σ-donor ability than other monoanionic ligands of second-row *p*-block elements such as C, N, and O.[18−24] If the boryl ligand is stabilized and acts as a "supporting" ligand, the strong electron-releasing property of the boryl ligand would be applied to functionalizations other than borylation.

To retain highly reactive anionic ligands on metal centers, multidentate ligands are generally utilized to take advantage of the chelate effect. Among them, PXP pincer ligands, meridional tridentate ligands shown in Figure 1, could provide remarkable thermodynamic stability to metal complexes.[25] Recent development of bulky and electron-rich phosphine-based PCP pincer ligands has disclosed unique

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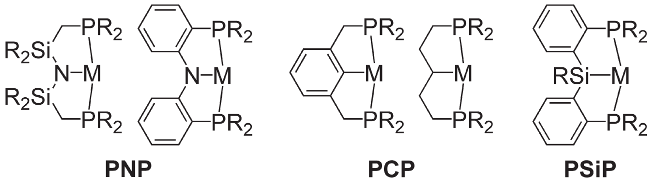
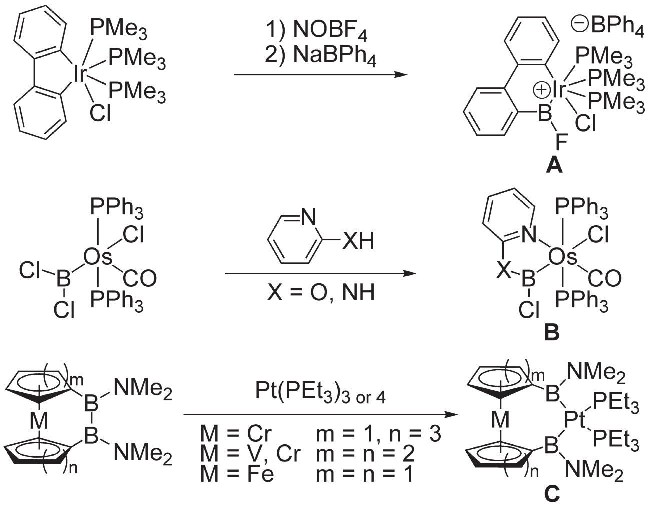


Figure 1. Representative PXP pincer complexes (X = N, C, Si).

Scheme 1. Formation of Transition Metal Complexes Bearing a Bidentate Boryl Ligand



reactivities of their iridium complexes toward the cleavage of C−H,[26−32] N−H,[33,34] and O−H[35] bonds.

However, there has been no attempt to obtain a tridentate boryl ligand precursor. Three examples of syntheses of transition metal complexes bearing a bidentate boryl ligand are shown in Scheme 1. The first structurally characterized transition metal complex having a bidentate boryl ligand is iridium complex **A**, which was generated via insertion of a boron atom into the C−Ir bond.[36] Rickard et al. reported complexation of 2-hydroxy- or 2-aminopyridine to (dichloroboryl)osmium to form bidentate boryl ligand-coordinated complexes (**B**).[37,38] Diborane(4)-bridged metallocene, which could be considered as a bidentate boryl ligand precursor, reacted with a platinum(0) complex via B−B oxidative addition to afford a series of platinum(II) complexes **C** having a bidentate diboryl ligand.[39−41]

On the other hand, boron-containing multidentate ligands with other coordination modes have also been recently developed. Most established examples are metal complexes, having a metal-to-ligand M−B σ-dative bond with one- (**D**),[42] two- (**E**),[43−48] or three (**F**)[47−65] tethered coordinating group(s). Compounds such as **F**, with a cage-like structure, are generally called “metallaboratoranes”. The other examples consist of metal complexes bearing a bidentate base-stabilized boryl ligand (**G**)[66] and a bidentate base-stabilized borylene ligand (**H**).[37]

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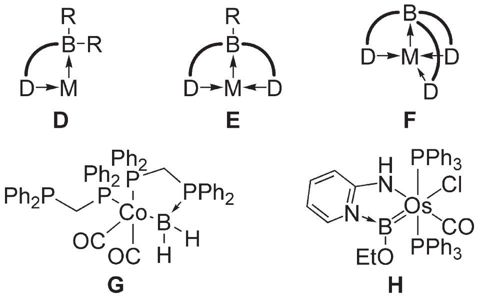
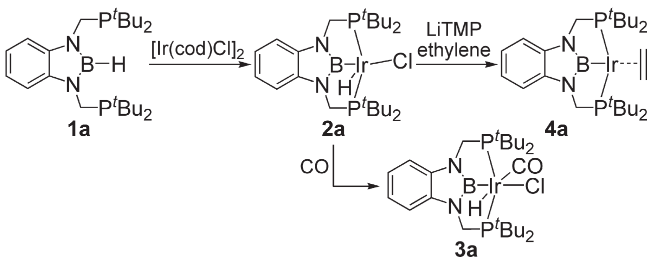
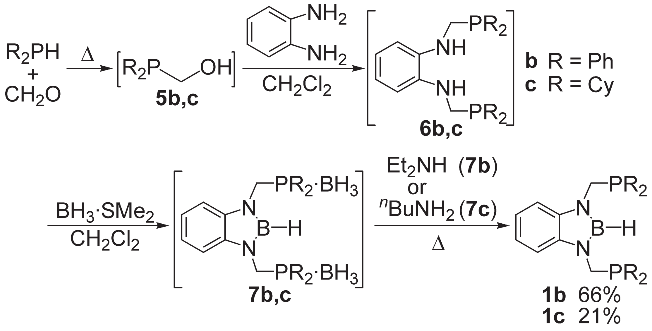


Figure 2. Previously reported transition metal complexes **D**−**H** bearing a boron-containing multidentate ligand.

Scheme 2. Syntheses of [^{t}BuPBP]Ir Complexes



Scheme 3. Syntheses of Hydroborane 1b,c



Recently, we have communicated the synthesis of PBP iridium complex **2a** by an oxidative addition of the B−H bond in **1a**, possessing di-*tert*-butylphosphinomethyl groups on nitrogen atoms. The resulting [^{t}BuPBP]Ir(H)Cl complex **2a** could be converted to [^{t}BuPBP]Ir(H)(CO)Cl complex **3a** and [^{t}BuPBP]Ir(C_2H_4) complex **4a** (Scheme 2).[67] Herein, we report further systematic study on the PBP iridium complexes, including the syntheses of hydroboranes with phenyl or cyclohexyl groups on their phosphorus atoms as PBP ligand precursors, their complexation with iridium to form iridium(III) complexes, solid state structures and DFT studies on the resulting complexes, and their conversion to the corresponding iridium complexes having an ethylene ligand.

Results and Discussion

Preparation of PBP Ligand Precursors. The synthetic route to hydroboranes **1b**,**c** bearing phenyl or cyclohexyl groups as PBP ligand precursors is shown in Scheme 3. Compounds **5b**,**c** and **6b**,**c** were synthesized according to the literature procedure (R = Ph).[68,69] Diphenyl- or dicyclohexylphosphine and paraformaldehyde were heated to afford oily products, which were hydroxymethylphosphines **5b**,**c** containing small amount of starting materials and byproducts (phosphine oxides). Condensation between **5b**,**c** and *o*-phenylenediamine took place at room temperature to give 1,2-bis(phosphinomethylamino)benzenes **6b**,**c**. Compound **6b** could be isolated in 63% yield as a colorless crystal, while **6c** was used for the next step without isolation. The crystal structure of **6b** is shown in Figure 3. Protons bonding to nitrogen atoms were surrounded by diphenylphosphino groups, and no hydrogen bonding was observed. Treatment of **6b**,**c** with 3.3 equiv of $BH_3 \cdot SMe_2$ afforded **7b**,**c** with formation of a benzodiazabororidine ring and protection of phosphines in one step. The deprotection of the phosphine-borane moiety of **7b**,**c** using diethylamine or *n*-butylamine proceeded without decomposition of the benzodiazaborole ring to give hydroboranes **1b**,**c** (**1b**: 66%, **1c**: 21%; from *o*-phenylenediamine). The characteristic proton signals bound to the boron atom (**1b**: 4.39 ppm, **1c**: 5.18 ppm) were detected by $^1H\{^{11}B\}$ NMR spectroscopy. The ^{11}B NMR chemical shifts of **1b**,**c** are around 25 ppm, which indicates that there is no Lewis acid−base interaction between boron and phosphorus atoms. Hydroboranes **1b**,**c** were crystallized from toluene/hexane at rt. The molecular structures of **1b**,**c** are shown in Figures 4 and 5. Hydrogen atoms on each boron atom were observed in the Fourier map, in which B−H bond lengths are around 1.1 Å. As indicated by NMR study, neither intra- nor intermolecular B−P Lewis acid−base interaction was observed in these solid state structures. No significant structural difference between each benzodiazabororidine moiety of **1b**,**c** has been observed.

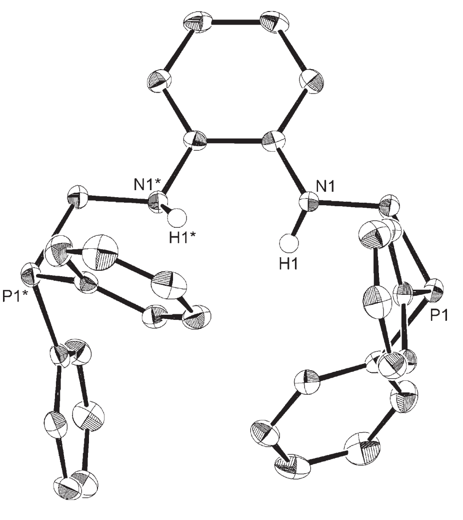


Figure 3. Crystal structure of **6b** (50% thermal ellipsoids; hydrogen atoms except N-H were omitted for clarity). Half of the entire structure constitutes an asymmetric unit where the numbers with asterisks are in the second asymmetric unit.

[PhPBP]Ir(H)(CO)Cl Complex 3b. Reactions of hydroborane **1b** bearing phenyl groups with various iridium(I) sources were examined (Scheme 4). Attempted synthesis of [PhPBP]Ir(H)Cl (**2b**) by the reactions with $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene), $[Ir(coe)_2Cl]_2$ (coe = *cis*-cyclooctene), and $[Ir(C_2H_4)_2Cl]_2$ afforded complicated mixtures. Reactivity of 1,3-$(Ph_2PCH_2)_2C_6H_4$ (PhPCHP) similar to **1b**

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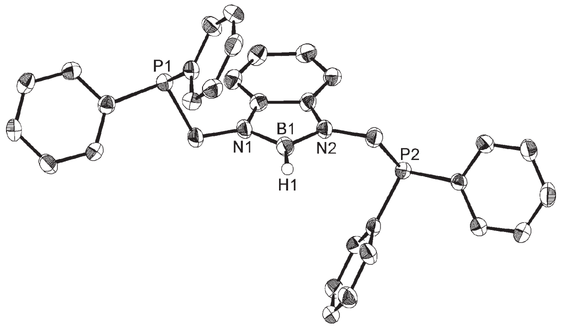


Figure 4. Crystal structure of hydroborane **1b** (50% thermal ellipsoids; hydrogen atoms except B-H were omitted for clarity).

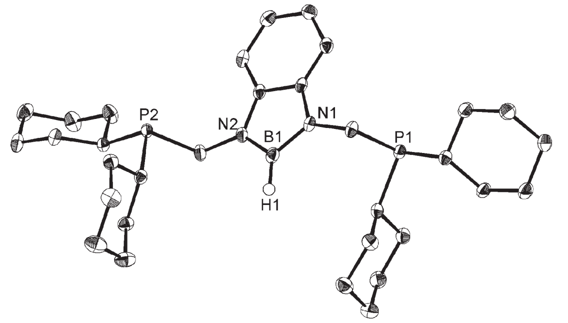
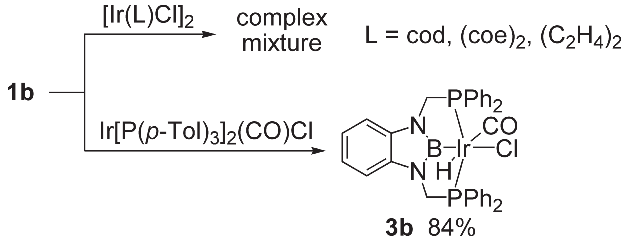


Figure 5. Crystal structure of hydroborane **1c** (50% thermal ellipsoids; hydrogen atoms except B-H were omitted for clarity).

Scheme 4. Reaction of Hydroborane 1b with Various Iridium(I) Sources



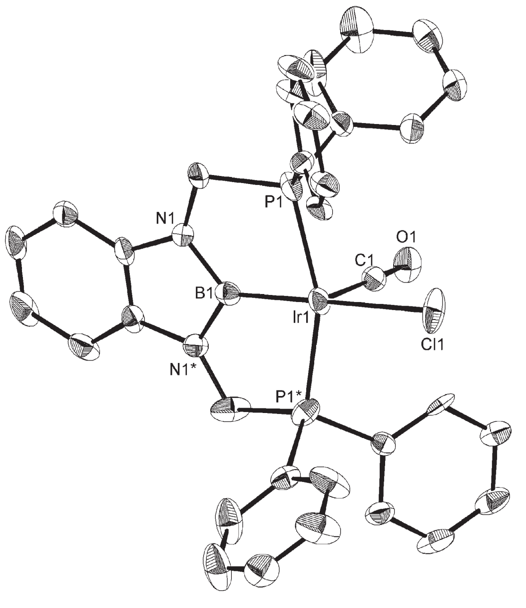


Figure 6. Crystal structure of **3b** (50% thermal ellipsoids; minor part of disordered moiety and hydrogen atoms were omitted for clarity). Half of the entire structure constitutes an asymmetric unit where the numbers with asterisks are in the second asymmetric unit.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 3b and 3a

	3b	3a
Ir−Cl	2.511(2)	2.5307(13)
Ir−B	2.010(8)	2.010(6)
Ir−C(1)	1.985(11)	1.923(5)
C(1)−O	1.155(11)	1.139(6)
Ir−P	2.313(2)	2.3546(13) 2.3588(13)
B−Ir−Cl	180	174.36(16)
P−Ir−P	156.92(7)	150.44(4)
Ir−C(1)−O	177.9(8)	179.3(5)
N−B−N	107.3(6)	106.3(4)

Table 2. Characteristic Peaks in the IR Spectra (cm^{-1}, KBr) of Complexes 3a,b and Reference Compounds 3a-opt, 3b-opt, and 8

	wavenumbers[a]	
3a[67]	1985(s)	2170(m)
3a-opt	1976(s)	2121(m)
3b	1994(m)	2091(s)
3b-opt	1977(m)	2073(s)

[a] s: strong, m: medium.

has been found by Yao et al.,[70] whereas the reaction of PhPCHP with [Rh(cod)Cl]$_2$ did not give [PhPCP]Rh(H)Cl, but did afford a mixture of dinuclear complexes. This is probably due to an inadequacy of steric bulkiness and/or electron donation, although the coordinatively unsaturated [^{t}BuPCP]Rh(H)Cl complex can be obtained from the reaction of 1,3-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_4$ (^{t}BuPCHP) with RhCl$_3$·H$_2$O[71] or [Rh(coe)$_2$Cl]$_2$.[72] On the other hand, reaction with Ir[P(p-tol)$_3$]$_2$(CO)Cl at 100 °C gave 18-electron [PhPBP]Ir(H)(CO)Cl complex **3b**. A triplet hydride signal [−7.92 ppm, t, $^2J_{PH} = 18$ Hz] and a triplet carbonyl signal [177.4 ppm, t, $^2J_{PC} = 7$ Hz] in the ^{1}H and ^{13}C NMR spectra of **3b** indicated that these two nuclei were coupled with two magnetically equivalent phosphorus nuclei.

Recrystallization of **3b** from THF/hexane gave colorless crystals of **3b**. The ORTEP drawing is shown in Figure 6. A C_2 axis through B−Ir−Cl exists in the molecule, and a hydride and a carbonyl group are disordered, while the previously reported **3a** has pseudo-C_s symmetry. The hydride ligand could not be found in the Fourier map. The chloride ligand was located at trans position to boron in the solid state structure of **3b**. Selected bond lengths and angles of **3b** and previously reported **3a** are shown in Table 1. The Ir−Cl and Ir−P bond lengths of **3b** are slightly shorter than those of **3a**, although there is no significant difference in Ir−B length and the structure of the benzodiazabororidine moiety. Bond lengths of the carbonyl group in **3b** follow the tendency observed in CO stretching wavenumbers, where Ir−C(1) is longer and C(1)−O is somewhat shorter compared with those in **3a**.

The IR spectroscopy of **3b** showed the characteristic CO and Ir−H peaks at 1994 and 2089 cm^{-1}, as summarized for the previously reported compound **3a**[67] in Table 2. For

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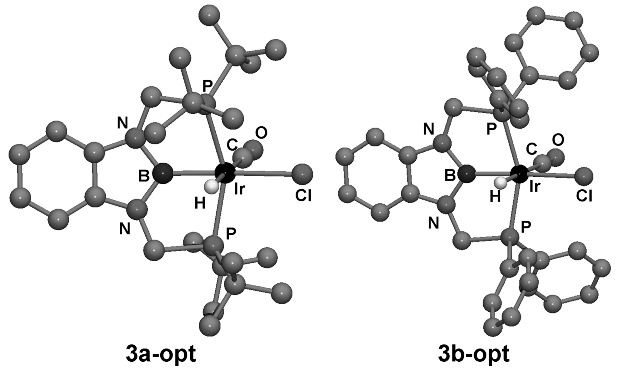


Figure 7. Structures of **3a-opt** and **3b-opt** (all hydrogen atoms except Ir-H were omitted for clarity).

comparison, theoretical calculation has been performed for **3a** and **3b**. Starting from the crystal structures of **3a** and **3b**, the optimized structures **3a-opt** and **3b-opt** were obtained by use of B3LYP/LanL2DZ/6-31G(d) calculations (Figure 7, structural parameters are found in the Supporting Information). The calculated structure of **3a-opt** well-reproduced the experimentally obtained structure of **3a**, while the structure of **3b-opt** has a pseudo-C_s symmetry compared with **3b**, possessing a C_2 axis along with B−Ir and Ir−Cl bonds. Results from vibrational analyses for **3a-opt** and **3b-opt** are also shown in Table 2.[73]

The ν_{CO} peak of **3b** had a slightly higher wavenumber and the ν_{IrH} vibration appeared at significantly lower wavenumber compared with those in **3a** (1985 and 2170 cm^{-1}). The higher wavenumber of ν_{CO} in **3b** than that of **3a** may be explained by a difference in electron density on the metal center. On the other hand, the calculation showed similar ν_{CO} values for **3a-opt** and **3b-opt** probably due to the structural difference between **3b** and **3b-opt** as described above. It is also noteworthy that the relative intensities of these two peaks in **3b** are reversed from those in **3a**. Although the reason for the significantly lower wavenumber of ν_{IrH} in **3b** compared to that of **3a** is not clear so far, vibrational analyses in **3b-opt** could reproduce the experimental observation. Similarly, the reversal of intensities for two peaks in **3a-opt** and **3b-opt** was also indicated by calculation, with a slightly smaller difference on ν_{IrH} peaks (48 cm^{-1}) compared to the experimental result (79 cm^{-1}). Considering force constants obtained from calculations on **3a-opt** and **3b-opt** (Figure 8), lower wavenumber peaks (a,c) can be assigned as a combination of H−Ir−C antisymmetrical stretching and C−O stretching. Higher wavenumber peaks (b,d) correspond to a combination of H−Ir−C symmetrical stretching and C−O stretching. Thus, the reversal of wavenumbers and peak intensities is attributable to the difference between the contribution of C−O stretching to ν_{IrH} peaks in **3a** and **3b**; namely, it may result from the difference in the donor abilities between Ph$_2$P and ^{t}Bu$_2$P groups or the conformational difference between **3a** and **3b**.

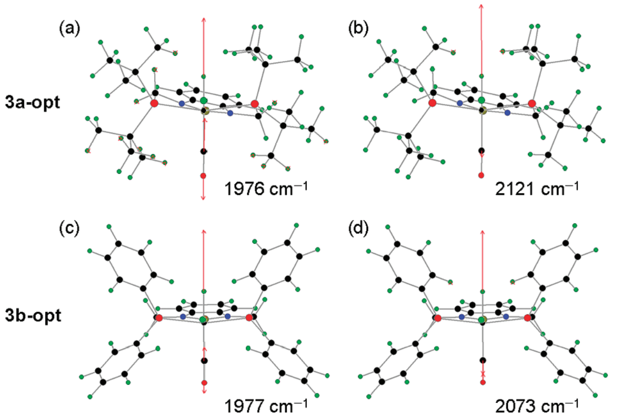


Figure 8. Vibrational modes for **3a-opt** (a,b) and **3b-opt** (c,d), where the red arrows show force constants.

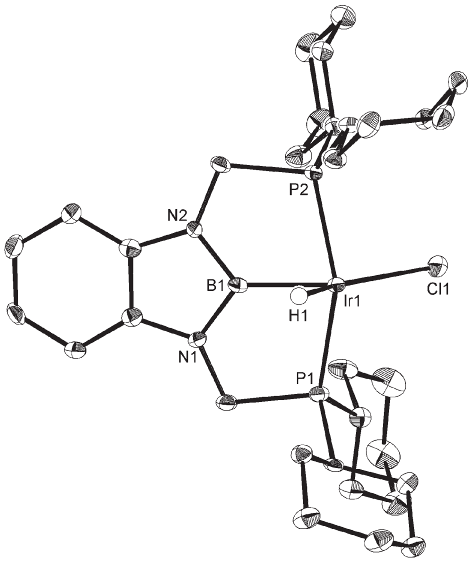
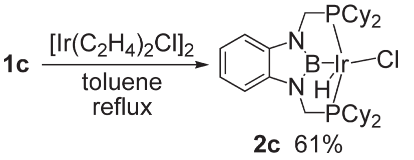


Figure 9. Crystal structure of **2c** (50% thermal ellipsoids; hydrogen atoms except Ir-H were omitted for clarity).

Scheme 5. Syntheses of [CyPBP]Ir(H)Cl Complex 2c



[CyPBP]Ir(H)Cl Complex 2c. Reaction of **1c** with [Ir(C$_2$H$_4$)$_2$Cl]$_2$ at toluene refluxing temperature forms [CyPBP]Ir(H)Cl complex **2c** with appearance of an Ir−H vibration [ν_{IrH}: 2361 cm^{-1}] in the IR spectrum (Scheme 5). The ^{31}P NMR chemical shift was shifted from −11.6 ppm (**1c**) to 63.4 ppm (**2c**) to show a complexation of the PBP ligand with iridium. The ^{11}B NMR signal showed a low-field shift from 25.9 ppm (**1c**) to 32.5 ppm (**2c**), which indicates formation of a B−Ir bond. The hydride of **2c** was observed as a sharp triplet due to coupling with two phosphorus atoms in its ^{1}H NMR [−26.19 ppm, t, $^2J_{PH}$ = 14 Hz in CD$_2$Cl$_2$] and was not sharpened by decoupling of the ^{11}B nucleus. These characteristics are similar to those of **2a**.[67]

A single crystal of **2c** was subjected to X-ray analysis. An ORTEP drawing is given in Figure 9, and selected bond lengths and angles of **2a,c** are summarized in Table 3. As expected, [CyPBP]Ir(H)Cl complex **2c** has a similar structure to previously reported [^{t}BuPBP]Ir(H)Cl complex **2a**. The position of the hydride ligand in **2c** was indicated by a Fourier map to be close [B−H = 1.90(5) Å] to the boron

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[73] Obtained vibration numbers were scaled with a factor of 0.961 for B3LYP/LanL2DZ calculations. See: NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101 Release 14, Sept 2006, Johnson, R. D., III, Ed.; http://srdata.nist.gov/cccbdb.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) of 2c and 2c-opt

	2c	**2c-opt**
Ir−Cl	2.3836(13)	2.467
Ir−B	1.979(5)	1.986
Ir−H	1.51(5)	1.591
B−H	1.90(5)	2.095
Ir−P	2.3103(13) 2.3109(13)	2.357
B−Ir−Cl	144.03(16)	136.9
P−Ir−P	157.11(4)	159.6
B−Ir−H	64.5(19)	70.7
Ir−B−H	45.6(15)	45.8
Ir−B−N	126.4(4) 126.8(4)	126.6
N−B−N	106.6(4)	106.8

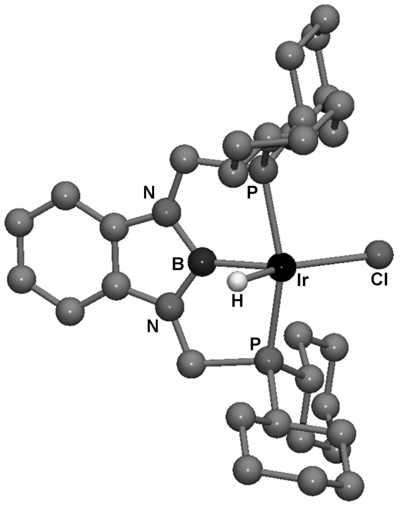
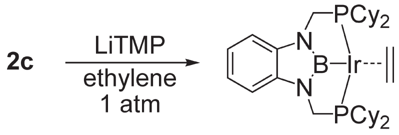


Figure 10. Structure of **2c-opt** (all hydrogen atoms except Ir-H were omitted for clarity).

atom. In the structure of **2c**, the central iridium atom formed a distorted trigonal-bipyramidal structure, consisting of two apical phosphine ligands and equatorial hydride, boryl, and chloride ligands with a small angle of B−Ir−H [64.5(19)°], as was observed in the structure of **2a** [63(2)°].[74] The sum of the three angles around the boron atom, not including the hydride, is 359.8°, indicating sp^2 hybridization of the boron center. The bent B−Ir−Cl angle in **2c** is about 14° smaller than that of **2a** probably due to the difference of steric hindrance between cyclohexyl and *tert*-butyl groups.

To clarify the position of the hydride ligand of **2c**, DFT calculations were performed with B3LYP/LanL2DZ/6-31G-(d). The crystal structure of **2c** was used as an initial structure for optimization, and the resulting structure of **2c-opt** is illustrated in Figure 10. Selected interatomic distances and angles are shown in Table 3. The Ir−H bond length in **2c** is slightly shorter than that in **2c-opt**.[75] In both **2c** and **2c-opt**, the hydride ligand is close to the boron atom [1.90(5) and 2.095 Å, respectively]. Similarly distorted trigonal-bipyramidal structures of (hydrido)(boryl)rhodium complexes (^{i}Pr$_3$P)$_2$Rh(H)(Cl)Bpin and Bcat[8,14] were investigated in-depth by X-ray, neutron diffraction, and DFT calculations, which showed a similar B−H separation of around 2.0 Å (neutron data).[76] As was concluded for the structure of **2a**,[50] **2c** could also be best described as (boryl)(hydrido)iridium(III) rather than (σ-borane)iridium(I) from a structural point of view, in addition to the ^{1}H{^{11}B} NMR experiment.

Scheme 6. Syntheses of [PBP]Ir(C$_2$H$_4$) Complex 4c



4c 81%

[PBP]Ir(C$_2$H$_4$) Complex 4c. The compound **2c** was converted to ethylene-coordinated iridium(I) complex **4c** by reaction with LiTMP under ethylene atmosphere (Scheme 6). A C_{2v} symmetrical structure of complexes **4c** was manifested by ^{1}H NMR spectroscopy, where four cyclohexyl groups were magnetically equivalent in C$_6$D$_6$ solution. The ethylene signal was observed as a singlet in the ^{1}H (2.77 ppm) and ^{13}C (38.1 ppm) NMR spectra. The low-field-shifted ^{11}B chemical shift (54.0 ppm) was in the typical range for boryl complexes, similar to that of **4a**.

In the crystal structure of **4c** shown in Figure 11, two ethylene carbons are almost coplanar to the plane defined by PBP and the central iridium atom. Although the bond lengths and angles around the ethylene ligand are quite similar to those of previously reported **4a**,[67] a significant difference was observed in the orientation of bulky alkyl groups on the phosphorus atoms. As shown in Figure 12, four *tert*-butyl groups of **4a** formed a C_2 symmetrical orientation, where two faces of the square plane are equivalent. On the other hand, a C_s symmetrical orientation was observed in the structure of **4c**. Thus, the central iridium atom of **4c** has a larger coordination sphere due to the smaller steric hindrance of the cyclohexyl groups compared to *tert*-butyl groups; even crystal packing may affect the orientation of the alkyl groups.

To observe the ethylene-coordinating intermediate, reactions of **2a**,**c** with ethylene gas were monitored by NMR spectroscopy (Scheme 7). Noteworthy, a significant difference was observed between **2a** and **2c**. A CD$_2$Cl$_2$ solution of **2a** under ethylene atmosphere did not show any spectral change except for the appearance of the dissolved ethylene signal. On the other hand, **2c** was quantitatively converted to the corresponding ethylene-coordinated complex **8c**. This may be explained by the larger coordination site of the [CyPBP]Ir complex to be occupied by ethylene. Dissociation of ethylene from **8c** to regenerate **2c** occurred under vacuum to prevent isolation of **8c**. The ethylene-coordinating

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[74] A distorted TBP structure possessing a small B−M−H angle has been reported with a related boryl(hydrido)rhodium chloride complex bearing two ^{i}Pr$_3$P ligands. See: (a) Lam, W. H.; Shimada, S.; Batsanov, A. S.; Lin, Z.; Marder, T. B.; Cowan, J.; Howard, J. A. K.; Mason, S. A.; McIntyre, G. J. *Organometallics* **2003**, *22*, 4557−4568. The reason for the formation of a small angle in the distorted TBP geometry of d^6-ML$_5$ complexes has been attributed to the lack of pπ−dπ interaction between two non-π-donor ligands such as hydrides and the central metal by Eisenstein with theoretical calculations. See: (b) Rachidi, I. El-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. (c) Riehl, J. F.; Jean, Y.; Eisenstein, O.; Pelissier, M. *Organometallics* **2002**, *11*, 729−737. So far, it is not clear why the "π-acceptor"' boryl ligand led to a similar geometry.

[75] It is often said "H is easy to locate through quantum calculations but hard to locate through experimental techniques"; we could believe the location of the hydride ligand generated by calculation rather than X-ray analysis. See: Maseras, F.; Lledos, A.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2000**, *100*, 601−636.

[76] Lam, W. H.; Shimada, S.; Batsanov, A. S.; Lin, Z. Y.; Marder, T. B.; Cowan, J. A.; Howard, J. A. K.; Mason, S. A.; McIntyre, G. J. *Organometallics* **2003**, *22*, 4557–4568.

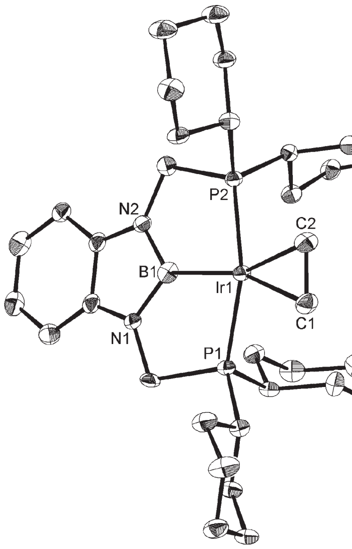
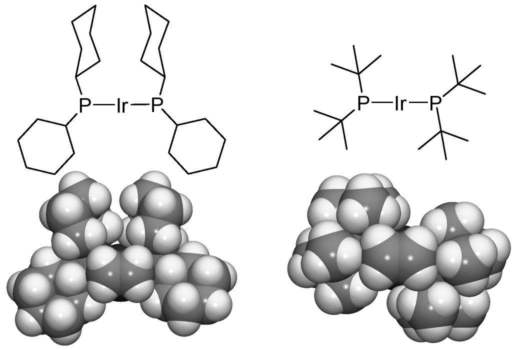


Figure 11. Crystal structure of **4c** (50% thermal ellipsoids; hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir−B, 2.069(5); Ir−C(1), 2.199(5); Ir−C(2), 2.181(5); Ir−P(1), 2.2808(13); Ir−P(2), 2.2821(13); C(1)−C(2), 1.405(7); B−N(1), 1.434(7); B−N(2), 1.431(7); C(1)−Ir−C(2), 37.42(19); Ir−C(1)−C(2), 70.6(3); Ir−C(2)−C(1), 72.0(3); P(1)−Ir−P(2), 144.86(5); B−Ir−C(1), 159.6(2); B−Ir−C(2), 158.7(2); N(1)−B−N(2), 104.8(4).

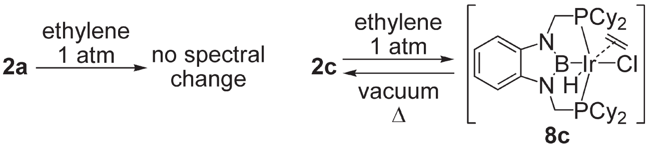


C_s symmetric
4c

C_2 symmetric
4a

Figure 12. Simplified structures of the orientation of bulky substituents on the phosphorus atom in **4a**,**c** with space-filling models.

Scheme 7. Difference in Reactivities of 2a and 2c toward Gaseous Ethylene and One Possible Structure of 8c



8c

complex **8c** was characterized by ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectroscopic data in CD_2Cl_2. The low-field ^{11}B signal of 48.0 ppm and one singlet ^{31}P signal of 38.9 ppm, which were obviously different from those of **2c** (δ_B: 32.5 ppm, δ_P: 63.4 ppm), indicated that the PBP ligand coordinated to the iridium center in a meridional fashion, where two phosphorus atoms are magnetically equivalent. Geminal coupling of two magnetically inequivalent methylene protons between N and P (two doublets at 3.78 and 3.96 ppm, $^2J_{HH}$ = 12 Hz) revealed a C_s symmetrical structure. The hydride was also detected as a triplet signal at high field (−26.32 ppm, $^3J_{PH}$ = 15 Hz) in the ^{1}H NMR spectroscopy. Coordinating ethylene signals were observed as a single peak in each of the ^{1}H and ^{13}C NMR spectra (3.20 and 49.4 ppm, respectively) distinct from a signal of dissolved free ethylene (5.38 and 112.1 ppm) at −90 °C. Coordinating and free ethylene signals were broadened due to rapid exchange at 20 °C. Although the relative configuration of hydride, chloride, and ethylene was not fully confirmed, chloride may be located at the trans position of the boryl ligand as was characterized for the structures of [PBP]Ir(H)(CO)Cl complexes **3a**,**b**. A boryl(hydrido)(alkene)metal species has been proposed as an intermediate of transition metal catalyzed hydroboration of an alkene[77] and was observed in a few examples before.[78−81]

Conclusion

Two hydroborane precursors (**1b**,**c**) for the PBP pincer ligand bearing phenyl or cyclohexyl groups on phosphorus atoms were synthesized. Although all the trials for complexation of phenyl-substituted hydroborane **1b** with chloroiridium(I) alkene complexes afforded complicated mixtures, reaction with Ir[P(*p*-tol)$_3$]$_2$(CO)Cl gave an 18-electron complex, [PhPBP]Ir(H)(CO)Cl (**3b**). The characteristic IR peaks in **3b** compared with the previously reported ^{t}Bu-PBP derivative **3a** were discussed on the basis of theoretical calculations. Introduction of the PBP ligand using cyclohexyl-substituted **1c** with $[Ir(C_2H_4)_2Cl]_2$ formed a 16-electron complex, [CyPBP]Ir(H)Cl (**2c**). The location of hydride atoms in **2c** was proven to be close to the boron atom, as suggested by a computational study, although no ^{11}B−^{1}H coupling was observed in the NMR study. Treatment of **2c** with base afforded the square-planar iridium(I) ethylene complex **4c**. Ethylene-coordinated iridium(III) complex [CyPBP]Ir(H)(C_2H_4)Cl (**8c**) could be observed as an intermediate in the formation of **4c**, in contrast to the case of **4a**, where no intermediate was detected, probably due to a difference in steric bulk. The observation of **8c** is a rare example of a spectroscopically identified boryl(hydrido)olefin metal complex.

Experimental Section

General Procedures. All manipulations were carried out in an argon-filled glovebox (Miwa MFG) unless otherwise noted. The ^{1}H, ^{1}H{^{11}B}, ^{11}B, ^{11}B{^{1}H}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on 500 MHz spectrometers with residual protiated solvent for ^{1}H and ^{1}H{^{11}B}, deuterated solvent for ^{13}C{^{1}H}, external $BF_3 \cdot OEt_2$ for ^{11}B and ^{11}B{^{1}H}, and external 85% H_3PO_4 for ^{31}P{^{1}H} used as reference. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, Graduate School of Science, The University of Tokyo. FAB-MS were measured on a JEOL JMS-700 mass spectrometer. Electrospray ionization-time-of-flight (ESI-TOF) mass spectra were recorded on a Micromass LCT KB 201 mass spectrometer.

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X-ray crystallographic analyses were recorded on a Rigaku Mercury CCD diffractometer. IR spectroscopies were measured on a Shimadzu FTIR-8400 and are uncorrected. Melting points were measured on a MPA100 Optimelt automated melting point system and are uncorrected. Ether, THF, and hexane were purified by passing through a solvent purification system (Glass Contour). Carbon monoxide (> 99.95 vol %) and ethylene (> 99.9 vol %) were obtained from Takachiho Chemical Industrial Co., Ltd. LiTMP,[82] Ph_2PCH_2OH (**5b**),[68] $[Ir(cod)Cl]_2$,[83] $[Ir(coe)_2Cl]_2$,[83] $[Ir(C_2H_4)_2Cl]_2$,[84] and Ir[P(*p*-tol)$_3$]$_2$(CO)Cl[85] were synthesized according to literature procedures.

Synthesis of 1b. A solution of **5b** (4.77 g, 22.1 μmol) and *o*-phenylenediamine (1.19 g, 11.0 μmol) in CH_2Cl_2 (50 mL) was stirred for 1 day. The resulting solution was filtered through a short silica column with 200 mL of THF, and then volatiles were evaporated to afford a colorless oil of **6b**. Then the oil was diluted with 100 mL of CH_2Cl_2. A solution of $BH_3 \cdot SMe_2$ (1 M in CH_2Cl_2, 100 mL) was added to the solution of **6c** at rt. The resulting solution was stirred for 12 h at room temperature. After solvents were evaporated under reduced pressure, THF (100 mL) and Et_2NH (30 mL) were added to the residue. The resulting Et_2NH solution was stirred for 12 h at refluxing temperature. After volatiles were evaporated under reduced pressure, the resulting suspension was filtered through a silica gel column with toluene (300 mL). An analytically pure sample was obtained from the recrystallization from Et_2O (3.74 g, 66% calcd from *o*-phenylenediamine). $^1H\{^{11}B\}$ NMR (C_6D_6, 500 MHz) δ 4.19 (d, $^2J_{PH}$ = 5 Hz, 4H), 4.39 (s, 1H), 7.00−7.04 (m, 12H), 7.12 (dd, J = 6, 3 Hz, 2H), 7.22 (dd, J = 6, 3 Hz, 2H), 7.28−7.31 (m, 8H); ^{13}C NMR (C_6D_6, 125 MHz) δ 45.8 (d, $^1J_{PC}$ = 12 Hz, CH_2), 110.5 (d, $^4J_{PC}$ = 5 Hz, CH), 119.7 (CH), 128.8 (d, $^3J_{PC}$ = 6 Hz, CH), 129.0 (CH), 133.4 ($^2J_{PC}$ = 18 Hz, CH), 137.8 (d, $^1J_{PC}$ = 15 Hz, 4°), 138.1 (4°); ^{31}P NMR (C_6D_6, 202 MHz) δ −21.8 (s); ^{11}B NMR (C_6D_6, 160 MHz) δ 25.2 (br s); mp 134.5−135.5 °C. Anal. Calcd for $C_{32}H_{29}BN_2P_2$: C, 74.72; H, 5.68; N, 5.45. Found: C, 74.51; H, 5.96; N, 5.39.

Isolation of 6b. A solution of **5b** (2.26 g, 10.4 mmol) and *o*-phenylenediamine (565 mg, 5.22 mmol) in CH_2Cl_2 (15 mL) was stirred for 1 day. The resulting solution was filtered through a short silica gel column with 100 mL of THF, and then volatiles were evaporated to afford a colorless oil. Addition of Et_2O (10 mL) to the oil led to the formation of a white precipitate, and the resulting solid was filtered. The crude product was dissolved in THF and recrystallized with THF/hexane to yield colorless crystals (1.66 g, 63%): ^1H NMR (C_6D_6, 500 MHz) δ 3.27 (s, 2H), 3.51 (d, $^2J_{PH}$ = 4 Hz, 4H), 6.68 (dd, J = 6, 3 Hz, 2H), 6.92 (dd, J = 6, 3 Hz, 2H), 7.02−7.03 (m, 12H), 7.34−7.37 (m, 8H); ^{13}C NMR (C_6D_6, 125 MHz) δ 44.0 (d, $^1J_{PC}$ = 11 Hz, CH_2), 113.2 (CH), 120.3 (CH), 128.9 (CH), 129.0 (d, $^3J_{PC}$ = 4 Hz, CH), 133.2 (d, $^2J_{PC}$ = 18 Hz, CH), 137.5 (d, $^1J_{PC}$ = 13 Hz, 4°), 138.1 (d, $^3J_{PC}$ = 7 Hz, 4°); ^{31}P NMR (C_6D_6, 202 MHz) δ −17.9 (s); mp 121.1−123.0 °C. Anal. Calcd for $C_{32}H_{30}N_2P_2$: C, 76.18; H, 5.99; N, 5.55. Found: C, 75.97; H, 6.13; N, 5.33.

Synthesis of 1c. A suspension of Cy_2PH (6.59 g, 33.2 mmol) and paraformaldehyde (998 mg, 33.2 mmol) was stirred for 4 h at 130 °C to afford a colorless oil. A solution of *o*-phenylenediamine (1.80 g, 16.6 mmol) in CH_2Cl_2 (100 mL) was added to the oil, and the resulting solution was stirred for 3 days. The reaction mixture was filtered through a short silica gel column with 300 mL of THF, and all the volatiles were removed under reduced pressure to afford a colorless oil (**6c**). A solution of $BH_3 \cdot SMe_2$ (1.0 M in CH_2Cl_2, 55.0 mL, 55 mmol) was added to a solution of **6c** in CH_2Cl_2 (100 mL) at 0 °C. The resulting solution was stirred for 12 h at room temperature. After solvents were evaporated under reduced pressure, *n*-$BuNH_2$ (50 mL) was added to the residue. The resulting *n*-$BuNH_2$ solution was stirred for 24 h at refluxing temperature. After volatiles were evaporated under reduced pressure, the resulting suspension was filtered through a silica gel column with toluene (300 mL). An analytically pure sample was obtained from the recrystallization from Et_2O (1.90 g, 21% calcd from *o*-phenylenediamine). $^1H\{^{11}B\}$ NMR (C_6D_6, 500 MHz) δ 1.13−1.32 (m, 20H), 1.52−1.83 (m, 24H), 3.91 (d, $^2J_{PH}$ = 3 Hz, 4H), 5.18 (s, 1H), 7.18 (dd, J = 6, 3 Hz, 2H), 7.45 (dd, J = 6, 3 Hz, 2H); ^{13}C NMR (C_6D_6, 125 MHz) δ 26.9 (CH_2), 27.6 (d, $^3J_{PC}$ = 2 Hz, CH_2), 27.7 (d, $^3J_{PC}$ = 4 Hz, CH_2), 29.9 (d, $^2J_{PC}$ = 11 Hz, CH), 30.2 (d, $^2J_{PC}$ = 12 Hz, CH), 33.6 (d, $^1J_{PC}$ = 17 Hz, CH). 40.2 (d, $^1J_{PC}$ = 19 Hz, CH_2), 110.6 (d, $^4J_{PC}$ = 5 Hz, CH), 119.4 (CH), 138.6 (4°); ^{31}P NMR (C_6D_6, 202 MHz) δ −11.6 (s); ^{11}B NMR (C_6D_6, 160 MHz) δ 25.9 (br s); mp 126.8−128.2 °C. Anal. Calcd for $C_{32}H_{53}BN_2P_2$: C, 71.37; H, 9.92; N, 5.20. Found: C, 71.21; H, 10.07; N, 5.12.

Synthesis of 3b. To a red solution of Ir[P(*p*-tol)$_3$]$_2$(CO)Cl (380 mg, 439 μmol) in toluene (7 mL) was added **1b** (226 mg, 439 μmol), and the resulting solution was stirred for 24 h at refluxing temperature to afford a pale yellow solution. Volatiles were removed from the solution, and the residue was reprecipitated from THF/hexane to afford an analytically pure sample (285 mg, 84%). Recrystallization from THF/hexane gave colorless crystals: ^1H NMR (C_6D_6, 500 MHz) δ −7.92 (t, $^2J_{PH}$ = 18 Hz, 1H), 3.91 (dvt, $^2J_{HH}$ = 12 Hz, $^2J_{PH}$ = 3 Hz, 2H), 4.46 (d, $^2J_{HH}$ = 12 Hz, 2H), 6.86−6.97 (m, 10H), 7.02 (t, J = 7 Hz, 4H), 7.11 (dd, J = 5, 3 Hz, 2H), 7.69 (dvt, $^3J_{HH}$ = 7 Hz, $^3J_{PH}$ = 5 Hz, 4H), 8.13 (dvt, $^3J_{HH}$ = 7 Hz, $^3J_{PH}$ = 5 Hz, 4H); ^{13}C NMR (C_6D_6, 125 MHz) δ 51.5 (vt, $^1J_{PC}$ = 25 Hz, CH_2), 110.0 (CH), 119.2 (CH), 128.8 (vt, $^3J_{PC}$ = 5 Hz, CH), 129.0 (vt, $^3J_{PC}$ = 5 Hz, CH), 130.7 (CH), 131.2 (CH), 131.4 (vt, $^2J_{PC}$ = 6 Hz, CH), 134.4 (vt, $^2J_{PC}$ = 6 Hz, CH), 137.0 (vt, $^1J_{PC}$ = 24 Hz, 4°), 140.2 (vt, $^3J_{PC}$ = 7 Hz, 4°), 177.4 (t, $^2J_{PC}$ = 7 Hz, 4°); ^{31}P NMR (C_6D_6, 202 MHz) δ 22.1 (s); ^{11}B NMR (C_6D_6, 160 MHz) δ 43.2 (br s); mp 166.8−169.4 °C (dec); IR (KBr) ν_{IrH} = 2089 cm^{-1}, ν_{CO} = 1994 cm^{-1}. Anal. Calcd for $C_{33}H_{29}BClIrN_2OP_2$: C, 51.47; H, 3.80; N, 3.64. Found: C, 51.67; H, 4.00; N, 3.45.

Synthesis of 2c. To a red solution of $[Ir(C_2H_4)Cl]_2$ (222 mg, 391 μmol) in toluene (15 mL) was added **1c** (421 mg, 781 μmol), and the resulting solution was stirred for 12 h at refluxing temperature to afford a red solution. Volatiles were removed from the solution, and the residue was reprecipitated from CH_2Cl_2/hexane to afford an analytically pure sample (356 mg, 61%): ^1H NMR (CD_2Cl_2, 400 MHz) δ −26.19 (t, $^2J_{PH}$ = 14 Hz, 1H), 1.21−1.55 (m, 22H), 1.71 (d, J = 3 Hz, 4H), 1.84 (br s, 8H), 1.98 (d, J = 12 Hz, 2H), 2.08 (d, J = 10 Hz, 2H), 2.23 (t, J = 12 Hz, 2H), 2.63 (t, J = 12 Hz, 2H), 3.36 (d, J = 12 Hz, 2H), 3.53 (d, J = 12 Hz, 2H), 6.98 (dd, J = 5, 3 Hz, 2H), 7.15 (dd, J = 5, 3 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 25.8 (CH_2), 26.0 (CH_2), 26.3 (vt, $^2J_{PC}$ = 6 Hz, CH_2), 26.5 (vt, $^2J_{PC}$ = 6 Hz, CH_2), 26.7 (CH_2), 27.1 (CH_2), 28.3 (CH_2), 29.4 (CH_2), 32.9 (vt, $^1J_{PC}$ = 12 Hz, CH), 34.1 (vt, $^1J_{PC}$ = 12 Hz, CH), 39.2 (vt, $^1J_{PC}$ = 20 Hz, CH_2), 107.2 (CH), 117.2 (CH), 139.1 (vt, $^3J_{PC}$ = 6 Hz, 4°); ^{31}P NMR (C_6D_6, 202 MHz) δ 63.4 (s); ^{31}P NMR (CD_2Cl_2, 202 MHz) δ 63.3 (s); ^{11}B NMR (C_6D_6, 160 MHz) δ 32.5 (br s); ^{11}B NMR (CD_2Cl_2, 160 MHz) δ 32.4 (br s); mp 186.0−189.7 °C (dec); IR (KBr) ν_{IrH} = 2361 cm^{-1}. Anal. Calcd for $C_{32}H_{53}BClIrN_2P_2$: C, 50.16; H, 6.97; N, 3.66. Found: C, 49.90; H, 6.92; N, 3.54.

Synthesis of 4c. Gaseous ethylene (1 atm) was introduced to a freeze−thawed solution of **2c** (600 mg, 783 μmol) in THF (10 mL). After stirring for 5 min at rt, a solution of LiTMP (127 mg, 862 μmol in 10 mL of THF) was added, and the resulting solution was stirred for 12 h at refluxing temperature. After volatiles were removed, Et_2O (100 mL) was added and

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resulting suspension was filtered through a Celite pad. After evaporation of Et_2O, recrystallization of the residue from Et_2O solution gave orange microcrystals (480 mg, 81%). Single crystals suitable for X-ray analysis were obtained from recrystallization with THF/hexane: ^{1}H NMR (C_6D_6, 500 MHz) δ 0.96−1.29 (m, 20H), 1.55 (d, J = 13 Hz, 4H), 1.60 (br s, 8H), 1.69 (d, J = 14 Hz, 4H), 1.94 (d, J = 8 Hz, 4H), 2.16 (t, J = 10 Hz, 4H), 2.77 (s, 4H), 3.70 (s, 4H), 7.07 (dd, J = 5, 3 Hz, 2H), 7.19 (dd, J = 5, 3 Hz, 2H); ^{13}C NMR (C_6D_6, 125 MHz) δ 27.2 (vt, $^2J_{PC}$ = 5 Hz, CH_2), 27.3 (vt, $^2J_{PC}$ = 6 Hz, CH_2), 29.4 (CH_2), 29.5 (CH_2), 36.9 (vt, $^1J_{PC}$ = 14 Hz, CH), 38.1 (CH_2, *ethylene*), 42.9 (vt, $^1J_{PC}$ = 21 Hz, CH_2), 108.3 (CH), 117.8 (CH), 140.9 (vt, $^3J_{PC}$ = 8 Hz, 4°); ^{31}P NMR (C_6D_6, 202 MHz) δ 69.8 (s); ^{11}B NMR (C_6D_6, 160 MHz) δ 54.0 (br s); mp 190.0−195.0 °C (dec); HRMS-ESITOF (*m*/*z*) $[M] + H^+$ calcd for $C_{34}H_{57}BIrN_2P_2$, 759.3719; found, 759.3341; $[M] + H^+ - C_2H_4$ calcd for $C_{32}H_{53}BIrN_2P_2$, 731.3406; found, 731.3430. Although the observed fragment peak of $[M] + H^+ - C_2H_4$ satisfied the calculated mass number, the parent ion $[M] + H^+$ was slightly different from calculation probably due to overlapping with a signal of impurity. Elemental analysis failed due to rapid decomposition of **4c**.

Observation of 8c. Gaseous ethylene (1 atm) was introduced to a freeze−thawed CD_2Cl_2 (0.6 mL) solution of **2c** (10.0 mg, 13.1 μmol) in a J-Young NMR tube at rt. The NMR tube was brought into an NMR probe and was cooled to −90 °C, and the reaction was immediately monitored by NMR spectroscopy. Complete disappearance of **2c** was observed, and formation of **8c** was confirmed by ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectra. ^{1}H NMR (CD_2Cl_2, 400 MHz, −90 °C) δ −26.32 (t, $^2J_{PH}$ = 15 Hz, 1H), 0.87−1.28 (m, 22H), 1.51−1.80 (m, 14H), 2.05 (s, 2H), 2.12 (s, 2H), 2.47 (s, 2H), 2.61 (s, 2H), 3.20 (4H, s, *coordinating ethylene*), 3.78 (d, $^2J_{HH}$ = 12 Hz, 2H), 3.96 (d, $^2J_{HH}$ = 12 Hz, 2H), 5.38 (s, *free ethylene*), 6.78 (dd, J = 5, 3 Hz, 2H), 6.83 (dd, J = 5, 3 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 24.7 (CH_2), 24.9 (CH_2), 25.2 (CH_2), 25.9 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 27.2 (CH_2), 32.3 (vt, $^1J_{PC}$ = 16 Hz, CH), 35.5 (vt, $^1J_{PC}$ = 11 Hz, CH), 39.2 (vt, $^1J_{PC}$ = 8 Hz, CH_2), 49.4 (CH_2, *coordinating ethylene*), 107.0 (CH), 116.2 (CH), 122.1 (CH_2, *free ethylene*), 137.5 (vt, $^3J_{PC}$ = 8 Hz, 4°); ^{31}P NMR (CD_2Cl_2, 202 MHz, 20 °C) δ 38.9 (s); ^{11}B NMR (CD_2Cl_2, 160 MHz, 20 °C) δ 48.0 (br s).

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **6b**, **1b**,**c**, **3b**, **2c**, and **4c** are listed in the Supporting Information. In each case, a suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) was used. The structures were solved by direct methods with (SIR-97)[86] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[87] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically in the difference Fourier maps or placed using AFIX instructions.

Computational Studies. The Gaussian 03 program[88] running on a SGI Altix4700 system was used for optimization (B3LYP/LANL2DZ for Ir, 6-31G(d) for others). Visualization of the results was performed by use of POV-Ray for Windows v3.5 software.

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Supporting Information Available: The details of X-ray and computational study, cif files, NMR spectroscopies, and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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